

Effect of Divalent Ions on the Structure of Organic Langmuir Monolayers

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Abstract No. Kmet2147

Beamline(s): X14A

Introduction: Langmuir monolayers of insoluble amphiphilic organic molecules at the air-water interface have been shown to influence the morphology and crystallographic orientation of a variety of inorganic crystals nucleated from the aqueous subphase [1]. The process of nucleation was rationalized mainly by assumptions about charge and stereochemical and geometric complementarity at the inorganic-organic interface. Distortions in the molecular structure of the organic Langmuir monolayer induced by the presence of metal ions in the aqueous subphase can be directly observed with grazing incidence diffraction and have been reported with calcium and cadmium ions [2,3]. Both ions distorted the hexagonal cell of the organic matrix, and in addition, superstructure peaks were observed with cadmium. The appearance, role and origin of the superstructure are not well understood, and systematic study of the effect of different ions is needed.

Methods and Materials: We have performed grazing incidence x-ray diffraction on Langmuir monolayers of heneicosanoic fatty acid (C_{21}) with chlorides of magnesium, lead, cobalt, copper in the aqueous subphase. The concentration of ions varied from 10^{-6} M to 10^{-3} M in steps of factor of 10 and pH from 6 to 10 in steps of 0.5. The monolayer was compressed to slightly above zero dynes/cm pressure and held at temperature of 10°C .

Results: Each ion induced a different distortion in the cell of the organic film as can be seen in Figure 1, and in addition, a series of small superlattice peaks was observed with magnesium and lead in the subphase as shown in Figure 2 for magnesium. The superstructures were commensurate with the organic lattice and indexed as 2×2 for magnesium ($4\times$ the area of the organic lattice) and for lead such that the superstructure had an area $14\times$ the area of the organic lattice. Lattice parameters of the oblique organic unit cell are shown alongside Figure 1. As can be seen from areas per organic molecule, magnesium had the greatest ability to pull the headgroups of the organic molecules together followed by lead, cobalt, and copper. Scans out-of-plane along each peak from the organic film (Bragg rods) confirmed that the organic molecules were all untilted when any of the ions was present in a slightly basic subphase ($\text{pH}>8$). These structures were sensitive to the concentration of the ion and pH as we recently reported for cadmium [4]. The 2×2 superlattice peaks for magnesium were the strongest in the pH 'window' between 8-9 and concentration of 10^{-4} M. For lead, all superlattice peaks could be clearly seen in the pH 'window' between 4-7 at a concentration 10^{-5} M. Concentration and pH values outside the 'window' would 'melt' the superstructure (for Mg^{2+} and Pb^{2+}) or the ions would leave the organic film in its usual low-pressure tilted phase (low concentration or low pH).

Conclusions: Unique variations in the organic unit cell show that every ion interacts with the organic monolayer differently. Structural relationships between inorganic crystal nuclei and the organic surface can now be deduced and provide insight into the rational for morphology and preferential orientation of mature crystals. Moreover, the fact that every ion induces a different structure in the organic monolayer means we now have a diffraction 'fingerprint' for an ion, and when there are two or more ions present in the subphase, we will be able to determine preferential binding and cation exchange at the interface.

Acknowledgments: This work was supported by the U.S. Department of Energy grant no. DE-FG02-85ER45125.

References: [1] S. Mann et al., *Science* **261**, 1286 (1993); [2] M.C. Shih et al., *J. Chem. Phys.* **96**, 1556 (1992); [3] F. Leveiller et al., *Langmuir* **10**, 819 (1994); [4] A. Datta, *J. Phys. Chem. B* **104**, 5797 (2000)

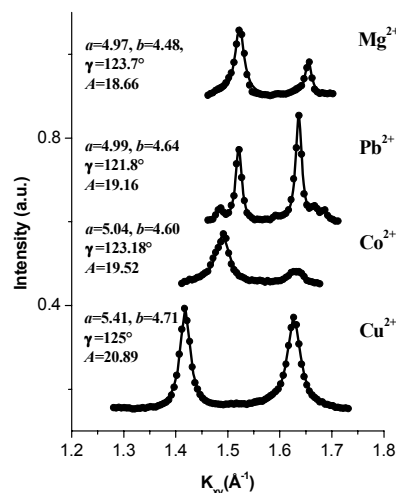


Figure 1. Diffraction pattern from Heneicosanoic acid monolayers with different ions in the subphase. Peaks shown are from the organic lattice. A few small superlattice peaks can be seen for lead in this K_{xy} region. Each ion induces a unique structure of the organic monolayer as is shown by the lattice parameters in the left column where a , b , γ are parameters of the oblique unit cell (in Å) and A is the area (in Å²).

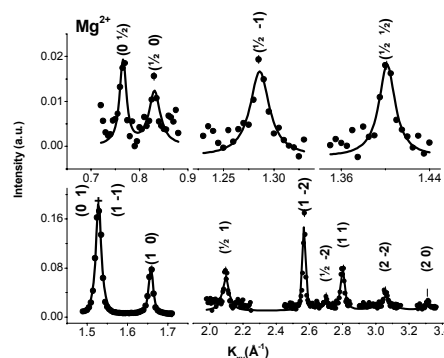


Figure 2. Diffraction pattern from Heneicosanoic acid monolayer with Magnesium ions in the subphase. The two peaks at ~ 1.5 and ~ 1.6 Å⁻¹ are from the organic lattice. The superlattice peaks correspond to a 2×2 superstructure of the organic lattice.